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# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### NO DRAWINGS

#### Improvements relating to Fuel Cells

We, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION, an Australian body corporate established under the Science and Industry Research Act, 1949, of 314 Albert Street, East Melbourne, in the State of Victoria, Commonwealth of Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in ion exchange membranes for use in membrane-type fuel cells.

This type of cell employs an ion exchange resin membrane, either cation or anion type, as a solid electrolyte which also serves to separate two electrode compartments. At one electrode fuel, either gaseous or liquid, is oxidized electrochemically, while at the other electrode oxygen (or air) is reduced electrochemically to promote the oxidation of the fuel. In a hydrogen/oxygen fuel cell with a cation-type membrane the electrode reactions are as follows:

ANODE  $2H_2 \longrightarrow 4H^+ + 4 \text{ electrons}$

CATHODE  $O_2 + 4H^+ + 4 \text{ electrons} \longrightarrow 2H_2O$

the overall reaction being

$2H_2 + O_2 \longrightarrow 2H_2O$

Other fuels which may be oxidized in a membrane-type fuel cell include hydrazine, methanol, formaldehyde, formic acid as well as carbon monoxide and some hydrocarbon gases such as propane. Oxygen as the oxidant gas may be replaced by air.

The above reactions will not proceed to an appreciable extent unless they are promoted by a catalyst, which is usually one of the noble metals such as platinum, palladium, iridium and rhodium. To be effective such catalyst must be prepared in an extremely finely-divided state (e.g. platinum "black") so that a large surface area is

exposed, with consequent increase in the number of sites at which the reactions can take place. As the cell reactions only take place at the catalyst surface the catalyst itself forms an electrode. Both the cathode and the anode are similarly formed and, in each case, a conductor for electrons, hereinafter called a collector, must be provided which is in intimate contact with the catalyst electrode and which thus serves to conduct electrons through an external circuit.

It is also essential for efficient operation at both electrodes that good contact be maintained between the ion exchange sites in the membrane and the catalyst electrode. In this way transport of hydrogen ions ( $H^+$ ) from the fuel catalyst through the membrane to the oxidant catalyst, where they are required for completion of the reaction, is promoted.

Early fuel cells of the membrane type used platinum (or platinum-plated) gauze on which platinum black was electrodeposited. These were pressed against the ion exchange membrane and acted as catalyst electrodes and also as collectors of electric current. Only small currents, of the order of 1 ma/cm.<sup>2</sup> of the electrode area, were produced from such cells. Later, membranes were developed in which the catalyst was incorporated into the surfaces of the membrane during final resin polymerization.

In the case of a hydrogen/oxygen cell employing a cation exchange resin membrane, the solid membrane electrolyte contains a solution of free acid, as acid-treatment is required to prepare the membrane for use. Also the free acid may assist in promoting migration of  $H^+$ . Each side of the membrane has a thin layer of catalytic "black" incorporated into its surface. Platinum black catalyst is usually chosen as being the most efficient for both electrodes.

[Price 4s. 6d.]

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The invention provides a method of producing an ion exchange membrane incorporating a metal catalyst for a membrane-type fuel cell, wherein the metal catalyst is deposited in a finely divided active state in a surface layer of the membrane by chemical reduction in situ of a salt of the metal.

Preferably the metal catalyst is a noble metal but other metals which can be produced by chemical reduction in their salts may also be employed.

In one embodiment of the invention an ionic reducing agent is absorbed on the membrane where it is used to reduce a metal salt in aqueous solution to the metal.

This procedure may be reversed in a further embodiment of the invention, wherein, an ion containing a metal is absorbed on the membrane and subsequently treated with a reducing agent.

The method of the invention also extends to the impregnation of an ion exchange membrane with a metal catalyst comprising two or more of the above mentioned metals, by deposition of the metals in the surface layer of the membrane by the above techniques.

By careful control of variables such as concentration of solutions, temperature and time of treatment, a layer of finely-divided active metal "black" is formed on both surfaces of the membrane. The thickness and depth of penetration of this catalyst layer can be controlled in such a way that efficient electrolytic contact with the membrane ionic sites is achieved, coupled with adequate catalyst loading and low surface resistance.

An advantage of the new process is that commercial membranes of different types, whether heterogeneous or homogeneous, can be quickly impregnated with the catalyst by varying the conditions to suit the type of membrane. This is of particular importance where the membranes are used in small quantities and are individually treated.

A further advantage of the process is the small weight of catalyst required per unit area of surface (degree of loading). Platinum black produced by this method has a high surface area per unit weight and efficient membranes have been prepared containing as little as a mg. of platinum/cm<sup>2</sup> of membrane surface. Low electrical resistance across the surface of the catalyst layer is important in providing efficient electron transfer between catalyst and collector, and the process has

the further advantage of being capable of producing catalyst layers whose surface resistance is less than 1 ohm/1 cm. × 1 cm.

It has been found that the reduction step is best carried out in neutral, alkaline or weakly-acid solution and that, whilst those membranes which have high water uptake absorb a relatively large amount of reductant or metal solution, membranes with low water uptake absorb only a small amount of such solutions. In this latter case it has been found that the amount of such solutions absorbed can be increased by drying the membrane before treatment and also that when only a small amount of reductant is absorbed, a heavier metal deposit is obtained by using a metal solution in which the metal in the ion is in a lower valency state; e.g. PtCl<sub>4</sub> -- (chloroplatinite) in place of the more usual PtCl<sub>6</sub> -- (chloroplatinate).

The following examples illustrate the method of the invention but it will be understood that no limitation of the scope of the invention is intended or implied thereby.

#### EXAMPLE I

A commercial heterogeneous cation exchange resin membrane having high water uptake (Permutit C20 (Permutit is a trade mark)), in the hydrogen form or in the sodium form, was immersed in a 15 per cent. solution of hydrazine hydrate at 50°C. for 30 minutes. Surplus hydrazine hydrate was removed by rinsing and the membrane was then immersed in a 3% solution of sodium chloroplatinate having a pH value of 3-4. Immersion time was 30 minutes at a temperature of 55-60°C. The membrane was then leached with water to remove free hydrazine and then leached with 1N H<sub>2</sub>SO<sub>4</sub> to ensure that cation sites were occupied by H<sup>+</sup> ions and to saturate the membrane with free sulphuric acid. The catalyst layers on each side of the membrane were shown by analysis to contain 2-3 mg. of platinum per cm<sup>2</sup>, in a finely divided state having a layer thickness of .01 - .05 mm. and surface resistance of 1.0 ohm/1 cm. × 1 cm.

In a hydrogen-oxygen fuel cell at room temperature with both gases at 2 p.s.i., the above membrane, held between two platinum gauze collectors, had an open circuit voltage of 1.06 v. and current could be drawn as follows:—

	10 ma/cm. <sup>2</sup> at 0.74 v. (corrected for iR voltage drop)				
20	"	"	0.60	"	"
30	"	"	0.42	"	"

**EXAMPLE II**

A commercial homogeneous cation exchange resin membrane of lower water up-  
take than that of Example I (made by  
5 Asahi Chemical Industries) in the hydrogen  
form, was dried at 65-70°C. for 30 minutes  
and then immersed in a 15% hydrazine  
hydrate for 16 hours at room temperature  
10 (removal of initial water by drying was  
found to increase absorption of hydrazine).  
After rinsing to remove surplus hydrazine  
hydrate the membrane was immersed in  
either (a) a 3% solution of  $\text{Na}_2\text{PtCl}_6$  adjusted  
with NaOH to pH 12, or (b) a 2.4% solu-  
15 tion of  $\text{Na}_2\text{PtCl}_6$  for 15 minutes at 55-60°C.  
The membrane was then leached with water  
followed by leaching with 1N  $\text{H}_2\text{SO}_4$  as in  
Example I.

The catalyst layers were shown by analy-  
20 sis to contain 2.5 mg. of Pt/cm.<sup>2</sup> and resist-  
ance of the surface was 1.2-2 ohms/1 cm.  
x 1 cm.

In the fuel cell of Example I at room tem-  
perature, open circuit voltage was 1.04 v.  
25 and a current of 10 ma/cm.<sup>2</sup> could be drawn  
at 0.59 v. (corrected for iR voltage drop).

**EXAMPLE III**

A commercial homogeneous cation ex-  
change resin membrane of low water up-  
30 take (American Machine & Foundry Co.  
313), in the hydrogen form, was dried at  
65-70°C. for 30 minutes and then immersed  
in 15% hydrazine hydrate for 16 hours at  
room temperature. After rinsing to remove  
35 surplus hydrazine hydrate the membrane  
was immersed in 2.4%  $\text{Na}_2\text{PtCl}_6$  at 55-60°C.  
for 15 minutes. A second treatment con-  
sisted of immersion in the above hydrazine  
hydrate solution at 50°C. for 30 minutes,  
40 rinsing to remove surplus hydrazine hydrate  
and immersion in 2.4%  $\text{Na}_2\text{PtCl}_6$  at 55-  
60°C. for 15 minutes. The membrane was  
then leached with water followed by leach-  
ing with 1N  $\text{H}_2\text{SO}_4$  as in Example I. The  
45 catalyst layers were shown by analysis to  
contain 1 mg. Pt/cm.<sup>2</sup> and resistance of the  
surface was 0.5-0.7 ohms/1 cm. x 1 cm.

In the fuel cell of Example I at room  
temperature, open circuit voltage was 1.02  
50 v. and a current of 10 ma/cm.<sup>2</sup> could be  
drawn at 0.58 v. (corrected for iR voltage  
drop).

Mixed noble metal catalysts were also  
deposited from chloride solutions by this  
55 method, and it was also found that with  
the very low surface resistance of the cata-  
lyst electrodes, the membrane could be made  
the cathode in an electrolytic cell and fur-  
ther catalyst deposits superimposed electro-  
60 lytically from pure or mixed metal chloride  
solutions. Such electrodeposits of mixed  
noble metals superimposed on chemically  
deposited catalyst layers were found to be  
65 effective electrodes in the hydrogen oxygen  
fuel cell and, in addition, effective for the

catalytic oxidation of formaldehyde in a  
formaldehyde-oxygen fuel cell.

**EXAMPLE IV**

A membrane of Example II (Asahi  
chemical Industries), after preparation of 70  
the catalyst layer by chemical reduction as  
quoted in the example, was made the cath-  
ode in an electrolytic cell containing a solu-  
tion of platinum and another noble metal,  
the total metal ion concentration being ap- 75  
proximately 1 per cent in 2N hydrochloric  
acid. At a current density of 12 ma/cm.<sup>2</sup>  
for 8 minutes at room temperature a mixed  
metal layer of fine structure was electro-  
deposited on to the chemically-deposited 80  
catalyst layer on each side of the mem-  
brane.

In a fuel cell similar to that described,  
but using a liquid fuel consisting of 1M  
formaldehyde in 0.5M  $\text{H}_2\text{SO}_4$ , the open cir- 85  
cuit voltage was 0.90 v. and a current of  
10 ma/cm.<sup>2</sup> could be drawn at 0.37 v.  
(corrected for iR voltage drop) at a tem-  
perature of 25°C.

**WHAT WE CLAIM IS:—**

1. A method of producing an ion ex- 90  
change membrane incorporating a metal  
catalyst for a membrane-type fuel cell,  
wherein the metal catalyst is deposited in a  
finely divided active state in a surface layer 95  
of the membrane by chemical reduction in  
situ of a salt of the metal.
2. A method as claimed in Claim 1,  
wherein the metal catalyst comprises a  
mixture of two or more metals. 100
3. A method as claimed in Claim 1 or  
Claim 2, wherein an ionic reducing agent  
is absorbed into the membrane and the  
membrane is then treated with an aqueous  
solution of the metal salt. 105
4. A method as claimed in Claim 1 or  
Claim 2, wherein an ion containing the  
metal is absorbed into the membrane and  
the membrane is then treated with a reduc-  
ing agent. 110
5. A method as claimed in any of the  
preceding claims, wherein the reducing  
agent is hydrazine or a derivative thereof.
6. A method as claimed in any one of  
Claims 1, 3, 4 and 5, wherein the metal 115  
catalyst is a noble metal.
7. A method as claimed in Claim 6,  
wherein the metal is platinum.
8. A method as claimed in any one of  
the preceding claims, wherein subsequently 120  
to the chemical deposition of the metal  
catalyst, a further amount of metal is elec-  
trolytically deposited in the membrane.
9. A method of incorporating a metal  
catalyst in an ion-exchange membrane sub- 125  
stantially as hereinbefore described with  
reference to any of the Examples I-IV.
10. A catalyst-impregnated ion-exchange  
membrane when produced by the method  
claimed in any one of claims 1 to 9. 130

11. A fuel cell incorporating an ion-exchange membrane according to claim 10.

KILBURN & STRODE.

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